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PRODUCTION OF PIGMENTS WITH PEROVSKITE-LIKE STRUCTURE BASED ON NICKEL ZIRCONATE BY THE PRECIPITATION METHOD

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The process of hydroxide coprecipitation of nickel(II) and zirconium(IV) yielding nickel zirconate are investigated. During subsequent thermal treatment of hydroxides under a lower temperature compared with powders, stabilized nickel zirconate is formed with a stable crystal lattice, in which Zr^{4+} ions are replaced by Ni^{2+} ions producing a tinted compound. This is a prerequisite for the synthesis of stable pigments with the perovskite-like structure.

The present study continues our research dedicated to the production of pigments with the perovskite-like structure using the method of precipitation from aqueous solution of salts [1 – 3]. In our experiments precipitates were synthesized, heat-treated, and used to produce pigments on the basis of the $NiO - ZrO_2$ system. The synthesis and the study of the pigments by DTA and x-ray phase analysis were performed similarly to our previous studies [1 – 3].

The initial materials were the following reactants: $NiSO_4$ ("pure"), $ZrOCl_2 \cdot 8H_2O$ ("chemically pure"), and ZrO_2 ("pure"). To prepare nickel zirconate, aqueous solutions of salts with a concentration of 0.5 M were prepared. They were mixed setting the $NiO : ZrO_2$ ratio equal to 1 : 1. Precipitation was performed using 1 M solution of NaOH ("pure") or NH_3 solution ("extra pure") diluted to 1 : 1. The solutions were poured together using the direct sequence of pouring. The optimum quantity of the precipitator was determined taking into account pH-titration data.

The precipitator was added to the system until reaching a pH value corresponding to the complete precipitation of ions, which was determined from the curves of pH-titration of salt solutions with alkali (Fig. 1) using a ÉV-74 pH-meter.

Analysis of titration curves suggests that until the formation of the solid phase the precipitating ions in the $Ni(II) - Zr(IV)$ system have a mutual effect on the hydrolytic properties of each other. Thus, the pH level of the formation of the joint precipitate $Ni(II) - Zr(IV)$ is lower than the pH of the precipitation of hydroxide $Ni(II)$ and higher than the pH of the precipitation of hydroxide $Zr(IV)$. In accordance with the solubility products, i.e., 2.0×10^{-15} for $Ni(OH)_2$ and 7.9×10^{-55} for $Zr(OH)_4$ [4], there should be two titration jumps on the curve of the titration of the mixed salt solution

with alkali, as a consequence of the consecutive precipitation of $Zr(OH)_4$ and $Ni(OH)_2$, which is in fact observed. However, the distorted course of the curve and the start of the second jump in a more acid range than that of curve 1 suggest that the hydroxide precipitate formed in the $Ni(II) - Zr(IV)$ system is a mixed chemical compound.

It should be noted that using aqueous ammonia solutions for precipitation makes the precipitate brighter due to the formation of nickel(II) ammoniate. However, when the precipitate is washed from an excessive precipitator, these relatively low-stability complexes are destroyed [4] due to the decreasing quantity of NH_3 . In using NaOH the precipitate of $Ni(II) - Zr(IV)$ is more gel-like.

The obtained precipitate after washing, filtering, and drying was investigated by the DTA method (Paulik – Paulik –

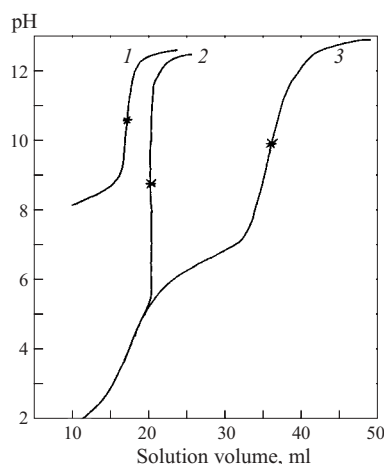


Fig. 1. Curves of pH-metric titration of solutions: 1) $Ni(II)$; 2) $Zr(IV)$; 3) $Ni(II) - Zr(IV)$; symbol "*" indicates the equivalence points corresponding to the completion of precipitation process.

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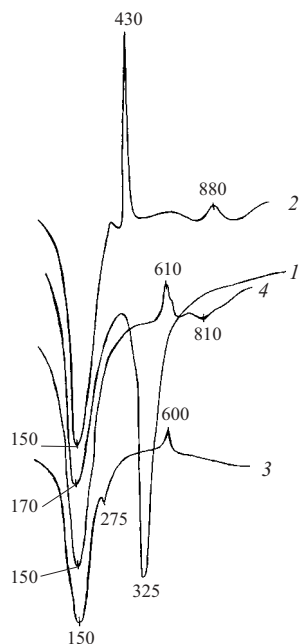


Fig. 2. Thermograms of hydroxide precipitates (°C): 1) Ni(II); 2) Zr(IV); 3) Ni(II) – Zr(IV); 1 – 3) precipitator NaOH; 4) Ni(II) – Zr(IV), precipitator NH_4OH .

Erday derivatograph, heating rate 10 K/min). The DTA curves are shown in Fig. 2, and the data on temperature intervals of the effects observed and respective weight losses of samples are specified in Table 1.

Nickel hydroxide is subjected to stepwise dehydration: first, crystallization water is removed, then structural water, the quantities of these two categories being commensurable, Zirconium hydroxide at a temperature of 150°C is subjected to dehydration, which is accompanied by subsequent crystallization of the tetragonal modification of ZrO_2 at a tempera-

ture of 430°C. With further increase in temperature up to 880°C a polymorphic transition of the tetragonal modification into the monoclinic one takes place.

Coprecipitated hydroxides Ni(II) – Zr(IV) obtained under the effect of alkali and ammonium are dehydrated at a temperature of 150°C, and the first sample is dehydrated stepwise. At a temperature of $605 \pm 5^\circ\text{C}$ the exothermic effect of crystallization is registered in both curves.

The DTA curves of the coprecipitated Ni(II) – Zr(IV) precipitates differ from the DTA curves of individual hydroxides. Compared to $\text{NiO} \cdot n\text{H}_2\text{O}$, the samples of $\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$ are dehydrated at a lower temperature and the curve does not have the endothermic effect at 325°C typical of $\text{NiO} \cdot n\text{H}_2\text{O}$. Compared to the DTA curve of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, the DTA curves of both samples of $\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$ do not have the exothermic effects of the tetragonal modification crystallization at 430°C or the polymorphic transition of the tetragonal modification into the monoclinic one at 880°C. All this suggests the interaction of nickel(II) and zirconium(IV) in the course of precipitation. Taking into account the significant difference in the acid-base properties of Ni(II) and Zr(IV) aqua-ions, one can assume the formation of nickel zirconate under the effect of both precipitators. This compound crystallizes at the temperature of $605 \pm 5^\circ\text{C}$, which is significantly higher than the temperature of crystallization of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$.

The total weight losses of samples $\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$ are equal to 37.0 – 38.2%, which exceeds the analogous data for individual hydroxides. The water content in the samples $\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$ does not obey the additivity rule, which also points to an interaction between the components [6].

TABLE 1

Compound	Temperature of peaks in DTA curve, °C	Temperature interval of DTA effect, °C	Weight loss		Energy effects
			%	quantity of H_2O , mole	
$\text{NiO} \cdot n\text{H}_2\text{O}$	170(–)	75 – 270	13.8	0.66	Dehydration
	325(–)	270 – 570	15.6	0.77	The same
	Total:	40 – 1000	29.6	1.75	–
$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$	150(–)	40 – 340	–	–	Dehydration**
	430(+)	380 – 480	22.9	2.0	Tetragonal modification crystallization**
	880(+)	780 – 930	–	–	Polymorphic transition of tetragonal modification to monoclinic**
$\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$	Total:	40 – 1000	24.1	2.2	–
	150(–)	20 – 260	37.0	6.5	Dehydration
	275(–)	260 – 370	–	–	The same
$\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}^*$	600(+)	550 – 650	–	–	Crystallization
	Total:	20 – 1000	37.0	6.5	–
	150(–)	20 – 490	33.0	5.4	Dehydration
$\text{NiO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}^*$	610(+)	550 – 690	1.6	0.2	Crystallization
	810(–)	740 – 850	2.0	0.2	Dehydration
	Total:	20 – 1000	38.2	6.8	–

* Sample obtained in precipitation using aqueous ammonia solution.

** According to data from [5].

Considering that the actual water content is higher than the quantity calculated by the additivity rule, one can assume the formation of solid solutions of hydroxide substitution [6].

After the synthesized precipitates were heat-treated for 1 h at 1100°C, they were studied by the x-ray phase analysis method on a DRON-3 set with ionization registration of scattered radiation (CuK_α radiation, 1000 pulses/sec, Geiger counter). The diffraction patterns (Fig. 3) were decoded using the JCPDS database (U.S.).

The diffraction patterns of calcined Zr(IV) hydroxide exhibits reflections belonging to different modifications of ZrO. Predominantly, ZrO exists in the monoclinic modification (3.24, 2.92, 2.60 Å). In addition, the reflections of a pseudocubic modification resembling the monoclinic one are registered (2.92, 1.85, 1.56 Å). The presence of NaOH sharply decreases the temperature interval of the transition of one modification into the other.

X-ray phase analysis of calcined Ni(II) – Zr(IV) samples indicates that when NaOH is used as a precipitator, the diffraction pattern exhibits reflections belonging to the cubic modification of ZrO_2 (2.97, 2.56, 1.82 Å) and NiO (2.10, 2.42, and 1.43 Å). Actually NiO stabilizes the monoclinic lattice of ZrO_2 , rearranging it into a cubic lattice. Such structure is not observed when NH_4OH is used as the precipitator. The diffraction patterns show the reflections of the monoclinic modification of ZrO_2 (3.20, 2.88, 1.82 Å) and NiO. In this case Ni^{2+} is not incorporated into the crystal structure of baddeleyite. Consequently, it is better to use the alkali as the precipitator, since it affects the rearrangement of the crystal structure.

Thus, the methods of DTA and x-ray phase analysis validate the formation of solid solutions of the perovskite type. Coprecipitated hydroxides in the course of subsequent heat treatment at a lower temperature than that of powder materials produce stabilized nickel zirconate with a stable crystal lattice, in which Zr^{4+} ions are replaced by Ni^{2+} ions with the formation of a tinted compound. This is a basis for the synthesis of stable pigments with the perovskite-like structure.

After heat treatment the precipitate obtained was used to produce pigments, which in a flux melt typically have lettuce-green tinting. The predominant wavelength is 573 nm and the tone purity is 37.5%.

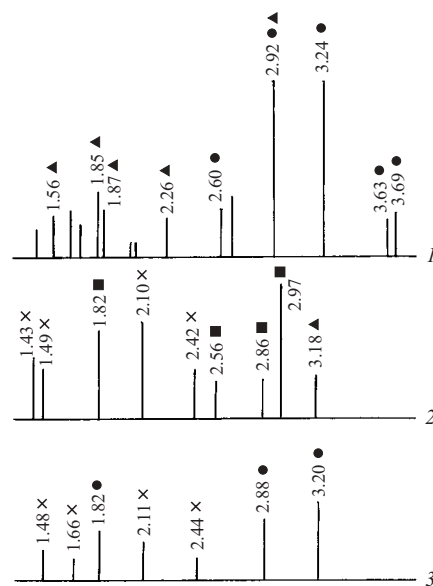


Fig. 3. Diffraction patterns of calcined hydroxide precipitates (Å): 1) Zr(IV); 2) Ni(II) – Zr(IV); 1, 2) precipitator NaOH; 3) Ni(II) – Zr(IV), precipitator NH_4OH ; ●) ZrO_2 of monoclinic modification; ■) ZrO_2 of cubic modification; ▲) ZrO_2 of pseudocubic modification; x) NiO.

REFERENCES

1. I. V. Pishch and E. V. Radion, "Synthesis of pigments based on perovskite," *Steklo Keram.*, No. 9, 23 – 24 (1998).
2. I. V. Pishch and E. V. Radion, "Specifics of precipitation and pigment formation in titanium – nickel – zinc system," *Steklo Keram.*, No. 10, 17 – 19 (1998).
3. I. V. Pishch and E. V. Radion, "Production of pigments with perovskite-type structure based on nickel titanate by precipitation," *Steklo Keram.*, No. 5, 30 – 32 (2003).
4. Yu. Yu. Lur'ye, *Reference Book on Analytical Chemistry* [in Russian], Khimiya, Moscow (1989).
5. T. M. Ul'yanova, N. P. Krut'ko, and T. A. Zus'kova, "Precipitation of hydrogel with ZrO_2 fibers and production of ceramics on this basis," *Vestsi Akad. Navuk Belarusi, Ser. Khim. Navuk*, No. 4, 28 – 32 (1995).
6. V. P. Chalyi, *Metal Hydroxides* [in Russian], Naukova Dumka, Kiev (1972).